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## CERAMIC PIGMENTS BASED ON TECHNOGENIC WASTE PRODUCTS AND LOCAL RAW MATERIALS

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The possibility of using local raw materials and industrial waste products to develop technology for obtaining ceramic pigments is investigated. Mix compositions have been developed for black, blue, and rose colors based on pyroxene waste products, manganese ore and spent catalyst (colorants), and wollastonite concentrate (mineralizer). The properties of the pigments are presented.

**Key words:** local raw material, technogenic waste products, ceramic pigments.

The ceramic industry in Uzbekistan has been experiencing difficulties with raw materials resources in the last few years. Deliveries of refractory and high-melting clays from Ukraine, perlite from the Caucasus, and other materials from regions in the former Soviet Union have been curtailed. The development of new deposits of raw materials requires, as rule, large investments of capital. For this reason, it is more cost-effective to use technogenic wastes, making it possible to solve two problems — ecological and raw materials — at the same time.

The development of resource-conserving technologies for construction ceramic is based on the use of local clays and industrial waste products to replace conventional raw materials brought in from outside the region. In this connection the Institute of Materials Science and Scientific – Industrial Association “Fizika – Solntse” has developed a technology for obtaining decorative building facing, façade, and acid-resistant composite ceramic articles based on local clayey raw materials, technogenic wastes, and pigments.

Ceramic pigments are heat-resistant colorants which are ordinarily obtained using chemically pure substances. Because they are synthesized at high temperatures using materials which are in short supply ceramic pigments are the most expensive raw materials used in the production of ceramic articles. Many investigations of the production of ceramic pigments have sought ways to replace the conventional raw materials with less expensive ones [1 – 3].

The objective of our work is to develop mix compositions and technologies for producing ceramic pigments based on local raw materials and industrial waste products. The colorant, containing oxides of transition *d* elements ( $Mn^{2+}$ ,  $Cr^{3+}$ ,  $V^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Fe^{3+}$ ,  $Cu^{2+}$ , and others), consisted of manganese ore and pyroxene wastes from production at the Koitash ore field as well as wastes from nitrogen production — spent aluminum-cobalt-molybdenum catalyst (Samar-kand), which was mixed with a mineralizer containing CaO (VK-70 wollastonite concentrate from the “Koitsk” deposit).

The pigments were prepared as follows. The components of the pigment mix were ground together by wet grinding to fineness permitting passage through a No. 0063 grid with no more than 0.5% residue, dried at 80 – 120°C, and fired at 1080 – 1200°C with soaking for 2 h. Next, the sinter obtained was milled to fineness allowing passage through a 10,000 openings/cm<sup>2</sup> sieve with no more than 0.3% residue.

For example, manganese ore, pyroxene wastes, and secondary kaolin from the Angren deposit were used to obtain black ceramic pigment with low synthesis temperature. The chemical composition of the proposed pigment is as follows (%<sup>3</sup>): 35.09 – 37.30 SiO<sub>2</sub>, 5.50 – 6.00 Al<sub>2</sub>O<sub>3</sub>, 0.33 – 0.40 TiO<sub>2</sub>, 12.20 – 12.90 Fe<sub>2</sub>O<sub>3</sub>, 24.80 – 25.60 CaO, 1.00 – 1.10 MgO, 11.60 – 12.80 MnO, 0.58 – 0.64 Na<sub>2</sub>O, 0.48 – 0.50 K<sub>2</sub>O, 4.00 Gr<sub>2</sub>O<sub>3</sub>, 0.80 – 0.90 Sb<sub>2</sub>O<sub>3</sub>, and 0.20 – 0.27 SnO<sub>2</sub>.

### Properties of Black Pigment

Firing temperature, °C . . . . .	1200
Chemical stability, % . . . . .	99.1 – 99.5
Color. . . . .	Black

<sup>3</sup> Here and below — content by weight.

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Spent aluminum-cobalt-molybdenum catalyst, chromium oxide, strontium oxide, and boric acid were used to obtain blue ceramic pigment with high chemical stability and low firing temperature. The mix composition for blue pigment is as follows (%): 36.0–45.0 spent catalyst, 30.0–42.4 chromium oxide, 5.0–15.0 strontium oxide, and 9.0–14.5 boric acid.

#### Properties of Blue Pigment

Firing temperature, °C . . . . .	1180–1220
Chemical stability, %:	
in 35% NaOH . . . . .	98.1–98.5
in 4% CH <sub>3</sub> COOH . . . . .	98.3–98.6
Color . . . . .	Blue-turquoise

The pigment was added to the glaze in amounts ranging from 5 to 10% depending on the desired saturation of the color tone of the coating.

The color of the pigment ranged from turquoise to blue; it remains stable at high temperatures and can be used to obtain colored glaze and for decorating porcelain and faience articles and construction ceramic. The investigations showed that to obtain blue ceramogranite it is sufficient to introduce into the main uncolored mix a mixture of the colorant (spent catalyst) in amounts 8.75% and 3.8% of the mineralizer (wollastonite concentrate) over and above 100%.

Manganese ore, spent catalyst, wollastonite concentrate, and boron oxide were used to synthesize rose-colored pigment. The chemical composition of the rose pigment was as follows (%): 8.83–10.07 SiO<sub>2</sub>, 61.68–65.30 Al<sub>2</sub>O<sub>3</sub>, 1.59–1.66 Fe<sub>2</sub>O<sub>3</sub>, 4.73–6.04 CaO, 0.11–0.12 MgO, 0.06–0.08 K<sub>2</sub>O, 6.46–6.85 Na<sub>2</sub>O, 0–0.03 TiO<sub>2</sub>, 3.40–5.52 MnO, 0–2.00 B<sub>2</sub>O<sub>3</sub>, 1.96–2.07 CoO,

0.34–0.36 P<sub>2</sub>O<sub>5</sub>, 1.96–2.07 MoO<sub>3</sub>, 0.765–0.81 WO<sub>3</sub>, 2.04–2.16 SO<sub>3</sub>, 0.07–0.12 SnO<sub>2</sub>, and 0.25–0.41 Sb<sub>2</sub>O<sub>3</sub>.

#### Properties of Rose Pigment

Firing temperature, °C . . . . .	1150–1180
Tone purity, % . . . . .	36
Chemical stability, % . . . . .	99
Color . . . . .	Rose

Pigment with this composition is distinguished by high quality, including purity of the color tone and low production cost, and does not contain substances which are harmful to health. It permits solving the problem of recycling large quantities of wastes.

The technology developed makes it possible to obtain pigments with stable characteristics with the indicated changes of the chemical composition of the ingredients used.

The use of industrial waste products instead of the conventional expensive primary raw materials makes the production of ceramic pigments economically profitable.

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